

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Process for the Manufacture of Packing Materials and for Treating Casting Moulds

We, DEUTSCHE ERDOL-AKTIENGESellschaft, a Company recognised by German law, of Mittelweg No. 180, Hamburg 13, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In the manufacture of packing materials, especially those used for packing products which are sticky or become soft when heated, such as bitumens, tar products, resins, artificial resins, waxes, cements, pastes or slack wax, and in the treatment of casting moulds, it has been proposed, in order to render them suitable for those products, to treat packing materials of the usual type of metal, wood, paper, fibrous material, fabric or the like or casting moulds, with a solution of a soluble derivative of alginic acid and then to treat the impregnation or coating so as to convert it into an insoluble derivative of alginic acid. In accordance with this proposal a two-bath process is used. Thus, a preferred method consists in immersing, for example, a coarsely porous cloth or paper fabric, if desired, in the form of bags, into a dilute solution of sodium alginate and subsequently treating the fabric in a second bath with a solution of calcium chloride, whereby a coating of insoluble calcium alginate is formed.

The present invention provides a process of the above kind for the manufacture of packing materials of metal, paper or fabrics, or for coating the inner surfaces of casting moulds. In the process of this invention a packing material of metal, paper or fabric is impregnated or coated, or the inner surface of a casting mould is coated, with a solution containing a water-soluble derivative of alginic acid, a solvent nitrogenous substance capable of forming complexes with metal ions, and a metal salt which is soluble in the complex-forming substance and forms with alginic

acid and derivatives thereof water-insoluble metal alginates or which solution contains a water-insoluble metal alginate maintained in solution by the complex-forming substance, and the complex-forming substance is subsequently removed.

An advantage of the new process is that it can be carried out in a single bath, that is to say, the packing material, which has been impregnated or coated with the solution of the metal alginate in the complex-forming substance, is not treated with a solution in a second bath in order to render the impregnation or coating insoluble, but the insolubilisation takes place practically of its own accord due to the evaporation of the excess of the complex-forming substance during the drying operation.

As water-soluble alginic derivatives there may be used, for example, ethers, esters or salts, for example, alkali metal or ammonium salts of alginic acid.

Solvent nitrogenous substances capable of forming complexes are ammonia or amines, for example, ethylamine, butylamine, propylamine or triethanolamine.

Suitable metal salts, which are soluble in the complex-forming substances, and which form water-insoluble metal alginates with alginic acid and alginic acid derivatives are, for example, salts of zinc, copper, aluminium, cadmium, nickel, cobalt, chromium and manganese.

The preparation of the solutions is illustrated with reference to zinc alginate as an example. Starting advantageously from an ordinary commercial alkali alginate a solution, for example, of ammonium or sodium alginate is mixed with a mixture of zinc oxide, ammonium carbonate and ammonia. Alternatively, a solution of zinc chloride or zinc acetate may be run into a solution of an alkali alginate, whereby a precipitate of insoluble zinc alginate is formed, and the pre-

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5 cipitate is redissolved by the addition of ammonia. In another method of preparing such a solution a sodium alginate solution, for example, is mixed with a solution of zinc chloride and ammonium carbonate, and the ammonia required to dissolve the zinc alginate is liberated by the addition of sodium hydroxide. Other metal alginates which are insoluble in water, but soluble in ammonia can be prepared in a similar manner.

10 The ammoniacal alginate solutions so obtained are advantageously used at a concentration of 0.5 to 12 per cent by weight.

15 The impregnation or coating of packing materials or of the inner surfaces of the casting moulds can be carried out by the methods customary for this purpose, such as immersion, spraying or rolling.

20 The coatings or impregnations are most simply converted into the water-insoluble form by exposure to air. In the production of packing materials on the large scale this insolubilisation is advantageously accelerated by heating and/or by a current of air. Heating is advantageously carried out by infra-red radiation, or by passing a current of air over the material and passing the latter through a heated tunnel. Alternatively, the packing material, treated with a solution, may be passed over heated rollers. The latter method has the advantage that the usual apparatus available in paper manufacture can be used. As it is also necessary in the known methods to dry the material which has been treated with the aqueous alginate and calcium chloride solutions, the removal of ammonia in addition to drying in the present process does not involve any substantial additional operations.

35 The degree of dryness of the coating of the insoluble derivative of alginic acid on the packing material may vary within wide limits. It may be adjusted by the addition of a hygroscopic substance such, for example, as glycerine, glycol or sorbitol. These substances or other substances for improving or modifying the properties of the coating may be added as in the known processes. As substances of this type may be mentioned apart from hygroscopic substances, substances that impart plasticity and elasticity, for example, starch in any stage of degradation, so-called soluble starch, dextrans, water-soluble cellulose ethers, plant mucilages, tragacanth and degradation products, of proteins. The solution may also contain a filler in fibrous or powdered form.

50 Packing material made in accordance with the invention permits of packing of substances that are sticky or soften when heated, such as bitumen, tar products or waxes, or of filling the packing material with such substances in a hot liquid state without packed substances penetrating into the paper or similar material, and without the packing material adhering firmly to the packed substance when the latter has solidified, so that

the packing material can only be removed with considerable effort from the packed substance and usually incompletely. In a similar manner substances that become soft or have been introduced at any desired temperature into casting moulds, which have been treated as described above, can easily be removed from the mould after cooling.

70 The following examples illustrate the invention, the parts being by weight:— 75

#### EXAMPLE 1.

2.5 parts of ammonium carbonate and 2.6 parts of zinc oxide are dissolved in 7.2 parts of a concentrated ammonia solution having a density of 0.88. 7.2 parts of ammonium alginate are dissolved separately in 110 parts of water. The ammoniacal zinc solution is stirred into this solution, preferably in a kneading machine with thorough mixing. A fluid viscous solution of zinc ammonium alginate is obtained. The solution is diluted with its own weight of water. A coarse paper tissue, such as is used for making potato bags, is immersed in the solution. The paper tissue is removed from the solution and dried for 15 to 20 minutes in a tunnel heated at 50° C. The paper then has a dense coating of water-insoluble zinc alginate.

#### EXAMPLE 2.

5.2 parts of zinc sulphate are dissolved in 10 parts of a concentrated ammonia solution of 0.88 density. 7.2 parts of sodium alginate are dissolved separately in 110 parts of water. The ammoniacal zinc sulphate solution is run slowly into the alginate solution, while mixing well in a kneading machine. A viscous homogeneous solution is obtained. 50 parts of this solution are mixed with 25 parts of water and 25 parts of glycerine. Paper may be treated with this solution in the manner described in Example 1.

#### EXAMPLE 3.

296 grams of ammonia solution of 25 per cent are added 148 grams of a zinc chloride solution of 20 per cent strength. The resulting solution containing the zinc bound in complex form is mixed with a solution of 100 grams of sodium alginate in 456 grams of water. The solution so obtained is diluted to an alginate content of 1 per cent (10 times). The material to be impregnated is immersed in diluted mixture and dried by infra-red radiation, after wiping off the excess solution.

#### EXAMPLE 4.

5.1 parts of copper sulphate are dissolved in 10 parts of a concentrated ammonia solution having a density of 0.88. The solution is slowly run into a solution of 7.2 parts of ammonium alginate in 110 parts of water. A homogeneous, viscous, deep blue solution of copper-ammonium alginate is obtained. An

alternative procedure is to mix together 3 parts of ammonium carbonate, 4 parts of sodium carbonate, 2 parts of copper sulphate and 2.5 parts of sodium alginate to form a dry powder, and to add 100 parts of water, while kneading. The solution is then diluted with its own weight of water. Coarse paper suitable for bags is immersed in the diluted solution. By treating the impregnated paper on cylinders heated at 100° C. there is obtained paper that is impermeable by viscous masses. When paper bags manufactured in that manner are filled with bitumen in a hot liquid state, the bitumen can easily be freed from the packing material, after cooling, when required for use.

#### EXAMPLE 5.

To 271 grams of a solution of 20 per cent strength of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are added 296 grams of ammonia solution of 25 per cent strength. The resulting solution containing copper bound in complex form is mixed with a solution of 100 grams of sodium alginate and 100 grams of glycol in 233 grams of water. The solution is diluted to an alginate content of 1 per cent (10 times). Paper to be impregnated is passed over rollers and sprayed with the impregnation solution in known manner, and subsequently heated on a heated roller and dried.

#### EXAMPLE 6.

296 grams of ammonia solution of 25 per cent strength are added to 199 grams of a solution containing 20 per cent of  $\text{CdCl}_2$ . The resulting solution containing cadmium bound in complex form is mixed with a solution of 100 grams of sodium alginate and 100 grams of sorbitol in 305 grams of water. The solution is diluted to an alginate content of 1 per cent (10 times). A material is impregnated with the diluted solution and dried as described in Example 1 or 3.

#### EXAMPLE 7.

A solution of 2 parts of sodium borate and 9 parts of ammonium carbonate in 100 parts of water is prepared. 1.5 parts of zinc sulphate are added to the solution and 2.5 parts of sodium alginate powder are added, while stirring vigorously. The sodium alginate is dissolved without the formation of a precipitate. A viscous solution is obtained which is then mixed with 80 parts of water. A casting mould is coated with the solution, and the coating is dried in the air. Bitumen which is introduced in a hot liquid state into the casting mould so treated can easily be removed from the mould, after cooling.

#### EXAMPLE 8.

440 grams of an ethylamine solution of 25 per cent strength are added to 148 grams of a zinc chloride solution of 20 per cent strength. The resulting solution containing

zinc in complex form is mixed with a solution of 100 grams of sodium alginate in 312 grams of water. The solution is diluted to an alginate content of 1 per cent (10 times). Fabric or paper to be impregnated is immersed in the solution and dried after wiping off the excess solution.

#### EXAMPLE 9.

3000 grams of an *n*-butylamine solution of 25 per cent strength are added to 148 grams of a zinc chloride solution of 20 per cent strength. The resulting solution containing zinc in complex form is mixed with a solution of 100 grams of sodium alginate in 6752 grams of water. The resulting solution contains 1 per cent of sodium alginate and is used for impregnation as described in Example 8.

#### EXAMPLE 10.

1774 grams of an *n*-propylamine solution of 50 per cent strength are added to 296 grams of a zinc chloride solution of 20 per cent strength. The resulting solution containing zinc in complex form is mixed with a solution of 200 grams of sodium alginate in 7730 grams of water. The resulting solution contains 2 per cent of sodium alginate and is used for impregnation as described in Example 8.

#### EXAMPLE 11.

2660 grams of an *n*-propylamine solution of 50 per cent strength are added to 296 grams of a zinc chloride solution of 20 per cent strength. The resulting solution containing zinc in complex form is mixed with a solution of 200 grams of sodium alginate in 6844 grams of water. The resulting solution contains 2 per cent of sodium alginate and is used for impregnation as described in Example 8.

It is also possible by adding to the solution a metal powder that reflects radiant heat, for example, aluminium, on the one hand, to reduce or largely inhibit the action of undesired radiant heat and, on the other, to achieve more rapid cooling by conduction, for example, when hot bitumen is poured into a casting mould coated with the solution.

In order to ensure satisfactory impregnation of coarse fabrics a pigment dyestuff or a soluble dyestuff may be added to the solution of the reaction components. Faulty places in the finished impregnated material can then easily be detected as more transparent areas when the material is held up to the light.

When the strength of the packing material is not of great importance, an unsupported film of a water-insoluble alginate may be used as a wrapping material. Such a film can be made, for example, by brushing or otherwise applying to a smooth surface, such as a roller or band, a solution of the reaction components (if necessary also with addition of fillers, metal powders or pigments), and subsequently removing the complex forming substance. After a certain period of drying the layer is

removed from the support. The resulting film can be used, for example, as an inner packing material or for wrapping goods directly.

WHAT WE CLAIM IS:—

- 5 1. A process for the manufacture of packing materials or for coating the inner surface of a casting mould by impregnating or coating a packing material of metal, paper or fabric or coating the said surface with a water-
- 10 soluble derivative of alginic acid and converting the alginic acid derivative in the impregnation or coating into an insoluble alginic acid derivative, wherein there is used for impregnating or coating a solution which
- 15 contains a water-soluble derivative of alginic acid, a solvent nitrogenous substance capable of forming complexes with metal ions, and a metal salt which is soluble in the complex-forming substance and forms with alginic acid
- 20 and derivatives thereof water-insoluble metal alginates or which solution contains a water-insoluble metal alginate maintained in solution by the complex-forming substance, and the complex-forming substance is subsequently
- 25 removed from the impregnation or coating to yield the insoluble metal alginate.
2. A process as claimed in Claim 1, wherein ammonia is used as the complex-forming substance.
- 30 3. A process as claimed in Claim 1 or 2, wherein the complex-forming substance is removed by the action of heat.
4. A process as claimed in Claim 1, 2 or 3,
- 35 wherein the metal salt or insoluble alginate is that of copper, zinc or aluminium.
5. A process as claimed in any one of

Claims 1—4, wherein the solution also contains a hygroscopic substance and/or a substance imparting plasticity and elasticity to the impregnation or coating.

6. A process as claimed in any one of Claims 1—5, wherein the solution also contains a filler in fibrous or powdered form

7. A process as claimed in any one of Claims 1—6, wherein the solution also contains a water-soluble dyestuff or a pigment.

8. A process as claimed in any of the preceding claims wherein the solution also contains a metal powder capable of reflecting radiant heat.

9. A modification of the process claimed in any one of Claims 1—8, wherein a self-supporting film suitable as a packing material is produced by applying a coating of the said solution to a support, subsequently removing the complex-forming substance, and then separating the resulting film from the support.

10. A process for the manufacture of a packing material or for coating the inner surface of a casting mould, conducted substantially as described in any one of Examples 1—11 herein.

11. Packing materials or self-supporting films which have been made, or casting moulds which have been treated, by the process claimed in any one of Claims 1—10.

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